

AD-A084 990

NAVAL RESEARCH LAB WASHINGTON DC

F/G 20/9

AN ASSESSMENT OF PHYSICS RESEARCH OPPORTUNITIES AVAILABLE FROM --ETC(U)

APR 80 J S MURDAY

NRL-MR-4211

SBIE-AD-E000 417

NL

UNCLASSIFIED

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

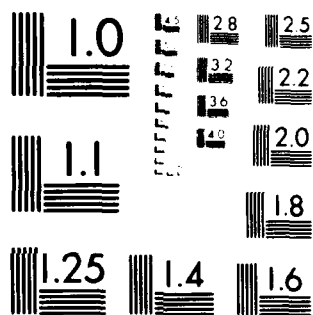
1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

1-1
A-100-100

END
DATE
FILMED
7 80
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

② LEVEL

**An Assessment of Physics Research Opportunities
Available from Rapid Heating and Cooling**

John S. Murray

**Surface Chemistry Branch
Chemistry Division**

ADA 084990

April 7, 1980

**DTIC
ELECTE
JUN 3 1980
S D B**



**NAVAL RESEARCH LABORATORY
Washington, D.C.**

Approved for public release; distribution unlimited.

80 4 14 023

FILE COPY

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER NRL Memorandum Report 4211	2. GOVT ACCESSION NO. AD-A084990	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) AN ASSESSMENT OF PHYSICS RESEARCH OPPORTUNITIES AVAILABLE FROM RAPID HEATING AND COOLING		5. TYPE OF REPORT & PERIOD COVERED Interim report on a continuing NRL problem.
7. AUTHOR(s) James S. Murday		6. PERFORMING ORG. REPORT NUMBER
8. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, D.C. 20375		9. CONTRACT OR GRANT NUMBER(s)
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Code 421, Attn: W. Condell Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61153N; RR011-02-03; 61-C001-X-0
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE April 7, 1980
		13. NUMBER OF PAGES 28
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Rapid heating Rapid cooling		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Rapid heating and cooling (i.e. rates of temperature change greater than 10^6 °K/sec) have become a major new approach to materials processing in the metallurgy and electronics communities; rates up to 10^{14} °K/sec have been reported in the literature. This report assesses where the capability for rapid energy transfer into a condensed phase, developed as part of materials processing research, might also be utilized to give new insights into physical properties or to explore new concepts in physics. The unique aspect of the rapid heating/cooling technology is the short time frame, 10^{-8} - 10^{-12} sec used to (Continues)		

DD FORM 1473
1 JAN 73

EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-014-6001

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

251 950

20. Abstract (Continued)

transfer the energy. Electron and laser beams are the most likely heating sources since they can generate short, intense, controlled pulses; rapid cooling must depend on conductive heat flow and is thereby restricted to thin film configurations. The perceived physics research opportunities are organized about four categories: mass transport, energy transport, theoretical concepts and dynamic measurement capability. The section on mass transport examines issues in nucleation, solidification, segregation, melting and metastable structure. The section on energy transport examines issues in beam-matter interactions, thermalization processes, interfacial energy transfer, thermoelectric effects, and thermoacoustic coupling.

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
DDC	Buff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
Dist.	and/or SPECIAL
A	

CONTENTS

I. INTRODUCTION	1
II. PHYSICS RESEARCH OPPORTUNITIES	6
A. Mass Transport: Kinetic Studies	6
1. Rapid Cooling	6
a. Rate of Nucleation	7
b. Kinetics of Growth — Crystalline vs Amorphous	9
c. Kinetics of Growth — Segregation and Alloy Solidification	10
d. Metastable Materials	10
2. Rapid Heating	11
a. Superheating-Melting	11
b. Kinetics Limited Transitions	11
B. Energy Transport	12
1. Beam Matter Interaction	12
a. Photon Beams	13
b. Electron Beams	13
c. Ion and Neutral Beams	14
2. Thermalization Processes: T_1, T_2	16
a. Electron-Phonon Thermalization	16
b. Phonon-Phonon Thermalization	17
3. Interfacial Energy Transfer	17
a. Solid-Gas	17
b. Solid-Solid and Solid-Liquid	18
4. Thermoelectric Effects	18
5. Thermo-Acoustic Coupling	18
C. Theoretical Concepts	19
D. Dynamic Analytical Capability	19
III. CONCLUSIONS AND RECOMMENDATIONS	22
REFERENCES	24

I. INTRODUCTION

There has been recent interest in the use of rapid heating or cooling as a mechanism for preparing specialized states of matter where rapid denotes rates of 10^4 K/sec and larger. This contrasts with typical laboratory heating and cooling rates which are in the range of 1° K/sec.

Rapid heating has been achieved through energy deposition from pulsed or from rastered CW sources. The two most common are IR-visible photon (laser) and electron beams; they can achieve subpicosecond and nanosecond pulse time, respectively. Both sources couple energy directly into the manifold of electron states. In condensed matter the energy is rapidly ($\sim 10^{-12}$ sec) equilibrated so that conventional treatments of rapid heating and cooling utilize the concept of temperature and macroscopic heat flow equations.

Rapid cooling is more difficult to achieve and is accomplished by conductive heat transfer. In order to achieve substantial cooling in short times, this technique is limited to thin layers in good thermal contact with a heat sink.

The desired magnitude of temperature change in rapid heating/cooling depends on the physical phenomena of interest. In studies of fusion by pellet implosion techniques, temperature changes of 10^5 °K and very short times are both desired. For beam weapons, the desired temperature range is $10^3 - 10^4$ °K; i.e., enough to create a plasma when the beam interacts with a surface. In the materials application area, the desired temperature changes are in the range $10^2 - 10^3$ °K; i.e., temperatures on the order of solid phase melting points. The various rapid heating and

Manuscript submitted February 21, 1980.

cooling regimes of technological interest are represented in Figure 1. The location of the features in Figure 1 will vary somewhat depending on energy source (laser wavelength, electron energy, etc.) and target material (specific heat, thermal conductivity, etc.), but the concepts are general.

The three examples cited in the previous paragraph are drawn from current technologies which seek to exploit the phenomena of rapid heating and cooling. Considerable research is presently funded in these areas with goals oriented toward a specific mission, i.e., fusion (DOE), weapons (DOD), and defect annealing/metastable materials (DOD, NSF). In these areas the research programs explore basic concepts in physics only insofar as to make progress toward the acquisition of the technological goal. There are considerable unexploited opportunities to use rapid heating and cooling to test our understanding of microscopic kinetic mechanisms, energy transfer, and nonequilibrium statistical mechanics. While the technologically oriented research programs may not adequately pursue the physics opportunities, they are critical to any basic research program in rapid heating and cooling because they contribute a pool of equipment, expertise, and phenomenology -- expensive resources needed for a viable basic physics research program.

The full range of phenomena which might be covered by a basic physics research program is far too extensive for a moderate budget. The laser fusion and beam weapons programs study the transformation from solid to plasma. The power density/pulse time characteristics of these programs lead to phenomena of specific interest to DOE and DOD, respectively. They are reasonably well funded and require large equipment investments. A

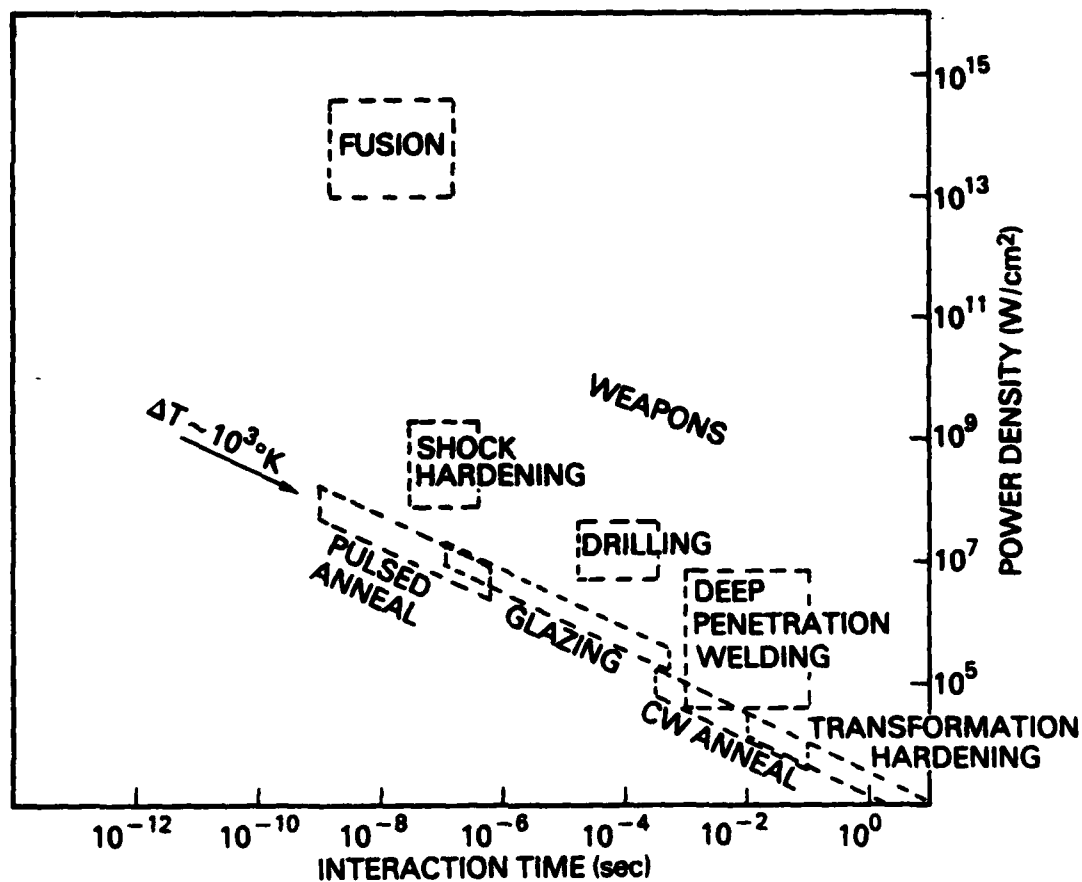


Fig. 1 - Operational regimes for laser techniques used for rapid heating/cooling. The dependence on the combination of applied power density and interaction time is here shown for a variety of commercial and experimental processes; the boundaries are approximate. (Adapted from B. H. Kear and E. M. Breinan in Needs and Opportunities for Basic Research in Laser Materials Interaction, National Science Foundation Report.)

limited ONR physics research program is not likely to make a major, clearly identifiable impact.

Rapid heating/cooling research for the region $T < T_{\text{vaporization}}$ has been largely directed toward the production of special material properties such as amorphous structures, metastable crystalline structures, enhanced solid solubility, reduced chemical segregation, refined grain sizes, refined second phase precipitates, and defect annealing. The funding is largely oriented toward materials research programs. There is considerable excitement in the materials community over opportunities for enhanced corrosion resistance, high strength alloys, improved electronic characteristics, new soft or hard magnets and other unique materials properties. There is also an opportunity here for a basic physics research program to make a significant contribution in a number of areas: study of microscopic kinetic processes as they relate to phase changes on mass transport and cooperative phenomena; study of relaxation processes which equilibrate the population of an excited manifold of states internally (T_2 processes) and externally (T_1 processes); study of heat flow across interfaces; and study of nonequilibrium statistical mechanics and the concept of temperature in the presence of large spatial energy gradients. The ability to exploit these opportunities will depend on our ability to get energy in and out of a material phase quickly and in a well-defined fashion; research will be needed here for better understanding of beam/surface interactions and heat transfer. The initial and final states of a condensed phase can be extensively studied at leisure with conventional bulk and surface analytical tools; full advantage of the physics opportunities will be realized only with the

development of dynamic analysis of temperature, composition, and structure.

In the next section these research opportunities will be illustrated in a little more detail.

II. PHYSICS RESEARCH OPPORTUNITIES IN RAPID HEATING/COOLING

A. Mass Transport: Kinetic Studies

The principal unique feature of rapid heating and cooling as defined here is the fast temporal behavior of the heating or cooling process. The beam energy sources provide the flexibility of choosing the temperature jumps and, to some extent, gradients. This provides the capability to study thermally activated kinetic processes with characteristic relaxation times τ which are on the order of or longer than the heating/cooling times t . Transient, nonequilibrium phenomena can be studied via impulse stimulation $t \ll \tau$ or fast steady state processes where $t \sim \tau$.

Depending on what phenomena one wishes to study, one may need either rapid heating or rapid cooling. The bulk of the discussion in this section is therefore organized relative to which is important. In many instances both rapid heating and cooling are used because one wishes either to (a) activate and then quench a thermal process in order to freeze in the change to provide time for analytical work, or (b) limit the high temperature region to surface layers.

1. Rapid Cooling

While there is considerable flexibility for injecting energy (heat) into a material, rapid cooling requires thermal diffusion into a heat sink. This limits rapid cooling studies to thin films, with faster cooling rates attainable only by ever smaller dimensions. The pico and subpicosecond laser pulses can deposit their energy in depths defined by the absorption coefficient.⁽¹⁾ With these depths and the available photon energy densities, it may be possible to achieve cooling rates up

to 10^{14} °K/sec ($dT/dx \sim 10^9$ °K/cm, thermal velocity $\sim 10^5$ cm/sec). If one approximates kinetic processes as being turned on or off by $\sim 10^2$ °K temperature changes, then relaxation times on the order of 10^{-12} sec and longer can be examined.

a. Rate of Nucleation

There have been several theoretical formulations of homogeneous nucleation as it relates to rapid heating and cooling.^(2,3) In all the theories the temperature dependence of the fluidity (diffusivity) between the melting temperature T_m and the glass transition temperature T_g is critical. An adequate estimate of this parameter is rarely experimentally or theoretically available. Davies⁽²⁾ has made some estimates for nucleation and growth of a vitreous phase for some elements and glass forming alloys; his predicted critical cooling rate R_c for vitrification is reported in Table 1. Reiss and Katz⁽³⁾ examine Cu and conclude that, given their estimate for fluidities, cooling rates $\sim 10^{12}$ °K/sec would be necessary, but that their fluidities were probably too large and a lower R_c might actually occur. Presently there is no experimental evidence which shows that nucleation in a pure metal has been prevented. More rapid quenching may show the effect. The microscopic role of alloying agents in nucleation could be better understood; studies at different quenching rates may provide information on the kinetics.

Whereas no pure metals have been quenched into an amorphous state, silicon has been retained in an amorphous state by rapid quenching from a molten state on top of an amorphous substrate. Perhaps silicon or other covalently bonded materials can be used to examine the concepts of fluctuation theory and promotion frequency (critical to stable nuclei

Table 1

The Liquidus (T_m), Glass Transition (T_g) or Crystallization (T_c) Temperatures and Predicted Critical Cooling Rate R_c for the Vitrification of Some Elements and Glass-Forming Alloys (Ref 2)

	T_m (K)	T_g or T_c (K)	T_g/T_m	R_c (Ks ⁻¹)
(1) Ni	1725	(425)	0.25	3×10^{10}
(2) Fe ₉₁ B ₉	1628	(600)	0.37	2.6×10^7
(3) Fe ₈₉ B ₁₁	1599	(640)	0.40	3×10^7
(4) Te	723	(290)	0.40	3.2×10^6
(5) Au _{77.8} Ge _{13.8} Si _{8.4}	629	293	0.47	7.4×10^5
(6) Fe ₈₃ B ₁₇	1448	760	0.52	10^6
(7) Fe _{41.5} Ni _{41.5} B ₁₇	1352	720	0.53	3.5×10^5
(8) Co ₇₅ Si ₁₅ B ₁₀	1393	785	0.56	3.5×10^5
(9) Ge	1210	(750)	0.62	5×10^5
(10) Fe ₇₉ Si ₁₀ B ₁₁	1419	818	0.58	1.8×10^5
(11) Ni ₇₅ Si ₁₈ B ₁₇	1340	782	0.58	1.1×10^5
(12) Fe ₈₀ P ₁₃ C ₇	1258	736	0.59	2.8×10^4
(13) Pt ₆₀ Ni ₁₅ P ₂₅	875	500	0.57	4×10^3
(14) Pd ₈₂ Si ₁₈	1071	657	0.61	1.8×10^3
(15) Ni _{62.4} Nb _{37.6}	1442	945	0.66	1.4×10^3
(16) Pd _{77.5} Cu ₆ Si _{16.5}	1015	653	0.64	320
(17) Pd ₄₀ Ni ₄₀ P ₂₀	916	602	0.66	120

transition) fundamental to homogeneous nucleation in a pure material. A key concept for examination would be the atomic jump frequency between nuclei and liquid states.

b. Kinetics of Growth-Crystalline vs. Amorphous⁽⁴⁾

The growth of a crystal into its melt occurs in a two-step sequence:

- (1) Rearrangement of the molecular configuration at the interface.
- (2) Transport of the heat of crystallization and any rejected impurity away from the interface.

All observations on the kinetics and morphology of growth of crystal into pure metal melts indicate that the interfacial rearrangement step is extremely rapid so that the overall process is controlled mainly by the rate of extraction of heat from the interfacial region. Spaepen and Turnbull⁽⁴⁾ suggest that the rearrangement step is close to the frequency of impingement of atoms from the fluid on the interface. Since this frequency is generally faster than diffusive or viscous frequencies, metals should crystallize even with undercooling to temperatures far below T_g . When impurity or alloy atom diffusive motion is required for crystal growth, then diffusive frequencies might become essential and this may account for the formation of amorphous alloys by rapid cooling. (See the correlation of R_c with T_g/T_m in Table 1. T_g is determined by the viscous frequency.) The details of this phenomena at the atomic level are only speculated.

Crystal growth in covalent systems is generally controlled by the rate of interfacial rearrangement. The temperature dependence of the rearrangement frequency usually follows an Arrhenius relation with

an activation enthalpy near the covalent bond energy. Spaepen and Turnbull speculate that impurity effects in crystallization may reflect their ability to catalyze or impede the rearrangement process.

c. Kinetics of Growth — Segregation and Alloy Solidification⁽⁵⁾

The inclusion of impurities in the resolidification wave front will depend on a balance between the rearrangement frequency necessary for incorporation into the lattice and the diffusive frequency. The velocity of the solid/melt interface will determine whether the impurity is engulfed by the interface or diffuses in front of it. Not much is known about the impurity rearrangement process nor about the effect of impurities on the rearrangement process of the host.

The growth kinetics in binary and higher alloy systems must also be determined by considerations similar to those involved in impurity segregation.⁽⁶⁾

d. Metastable Materials

The growth of amorphous layers and metastable crystalline structures by rapid cooling suggests that special metastable structures might be formed by rapid cooling techniques. There is evidence that films grown by some form of vapor phase deposition onto a substrate (an atomistic analog of rapid cooling or heating) can grow film structures not stable in bulk at the substrate temperatures. The production of these metastable materials could be very important, for superconductors for example⁽⁷⁾ and perhaps in magnetic or ferroelectric materials.

Rapid heating and cooling of films can also be used to create metastable states which could have special electronic, magnetic, or some other desirable property. IBM recently reported such work on magnetic

bubble materials.⁽⁸⁾ The ability to create very small hot zones via the beam devices could open possibilities for microdevice applications. The behavior of multi-element, non-metallic materials subjected to rapid heating/cooling processes is pretty much an unexplored area.

2. Rapid Heating

Rapid heating is important in those instances where one wishes localized heating, for instance heating surface films without changing bulk temperatures, or where one wishes to bypass kinetic processes which might dominate at lower temperature regimes.

a. Superheating-Melting^(9,10)

One theory of melting postulates that melting is essentially the reverse of solidification, i.e., that there is a nucleation barrier for melting which must be overcome. Surfaces or interfaces serve as nucleation sites for melting and make superheating difficult.⁽¹⁰⁾ Superheating has been demonstrated in a few instances where energy could be deposited so as to change the internal temperature fast compared to the progressing melt/solid interface. This implies viscous melts. The rapid heating capability, in particular electron beams which may be able to deposit energy preferentially away from the surface, might be able to look for any melting kinetics barrier. If there is a melting kinetics barrier, it must also play a role in calculating the heat transfer associated with laser or electron beam energy deposition.⁽⁹⁾

b. Kinetics Limited Transitions

There are phase transformations in the solid state which are composition invariant and can be thermally activated, for instance the so called massive transformations^(11,12) of which the martensitic transforma-

tion is an example. There is a lack of detailed kinetic formation about these transformations. Since they do not involve diffusive motions, they are fast and are good candidates for study by rapid heat or cooling.

A direct amorphous to liquid transition can require rapid heating so that the amorphous material does not first nucleate and grow a crystalline phase.⁽⁴⁾

Rapid heating of a reactant could place a material into a high temperature state where the reaction kinetics could be quite different than at lower temperatures. Studies of explosives in particular might lead to a different approach to studies of detonation.⁽¹³⁾

Rapid heating can lead to a different approach to annealing of lattice defects since the temperature-time regimes can be very different from conventional oven annealing. This approach is the subject of a large effort in semiconductor materials development.

B. Energy Transport

1. Beam Matter Interaction

The energy transfer from incident beam to substrate is of interest for three reasons. First, different mechanisms of absorption can lead to different materials response. Second, the properties of the incident particle itself might contribute to the materials response. For instance, a photon disappears upon absorption whereas an electron requires the dissipation or incorporation of a charged particle. Third, without a good understanding of the energy transfer it will not be possible to accurately calculate temperature profiles. Since these profiles are presently difficult to measure, one must rely heavily on the accuracy of these calculated values.

a. Photon Beams

The use of high power CW and pulsed lasers as sources of heat is widespread. The laser has two distinct technical advantages: (1) it can deliver power in very short times, i.e., nanoseconds for Q switched lasers and picoseconds for mode locked lasers, and (2) photon absorption in the metals and semiconductors where the penetration depth of IR and visible light is 10^{-4} - 10^{-6} cm leads to localized heating in the surface regions. This fact is important for the study of surface and film phenomena where much of the materials research is centered. Time resolution is an important part of the rapid heating/cooling research. The available pulse lengths for lasers are presently shorter than found for electron sources; shorter pulse lengths (~ 0.1 ps) are presently being investigated, but the prospects for even better time resolutions in the visible are small since the pulse length is approaching the photon wavelength.

The absorption of the photon energy is believed to be understood in principle. However, there is not detailed knowledge of the reflectivity as a function of temperature. This provides uncertainties in the heating input rates which are utilized to determine the temperature/time profiles.

b. Electron Beams (13,14)

The materials research is being pursued predominantly with laser beams; the reasons for this appear to be based on availability and cost. However, the total and local energy deposition into a material by a given laser are influenced by a number of materials factors such as surface roughness, crystallinity and composition. Energy desposition by electron

beam is by sequential inelastic scattering and depends essentially only upon electron energy and atomic composition of the target material. Variations in surface character, degree of crystallinity, etc. do not alter this scattering.

The distribution of electron beam energy deposited as a function of depth in a material is controlled by the beam voltage and angle of incidence (see Figure 2); it is readily conceivable that temperature profiles could be tailored by appropriate combinations of beams with different voltage. Ready control of lateral temperature distributions is also possible. These properties could make electron beam sources a more flexible heat source for technological application.

One other feature of the electron beam could be of importance. The energy deposition rate of a high energy electron beam is dependent on its kinetic energy, as it slows down, the rate increases. This could provide a mechanism for depositing energy in subsurface layers whereby the highest temperature would not be on the surface. Such a feature might be useful for superheating studies or other work where changes to the surface properties were not desired.

The appropriate electron beam sources presently available have time resolution $\sim 10^{-8}$ sec. Improvements in this pulse duration are desirable.

c. Ion and Neutral Beams

These sources of energy are not used due to (1) insufficient energy fluxes in the case of neutrals, (2) incorporation of foreign atoms in the materials of interest, and (3) damage to the substrate in the form of lattice destruction and sputtering. The penetration of a condensed

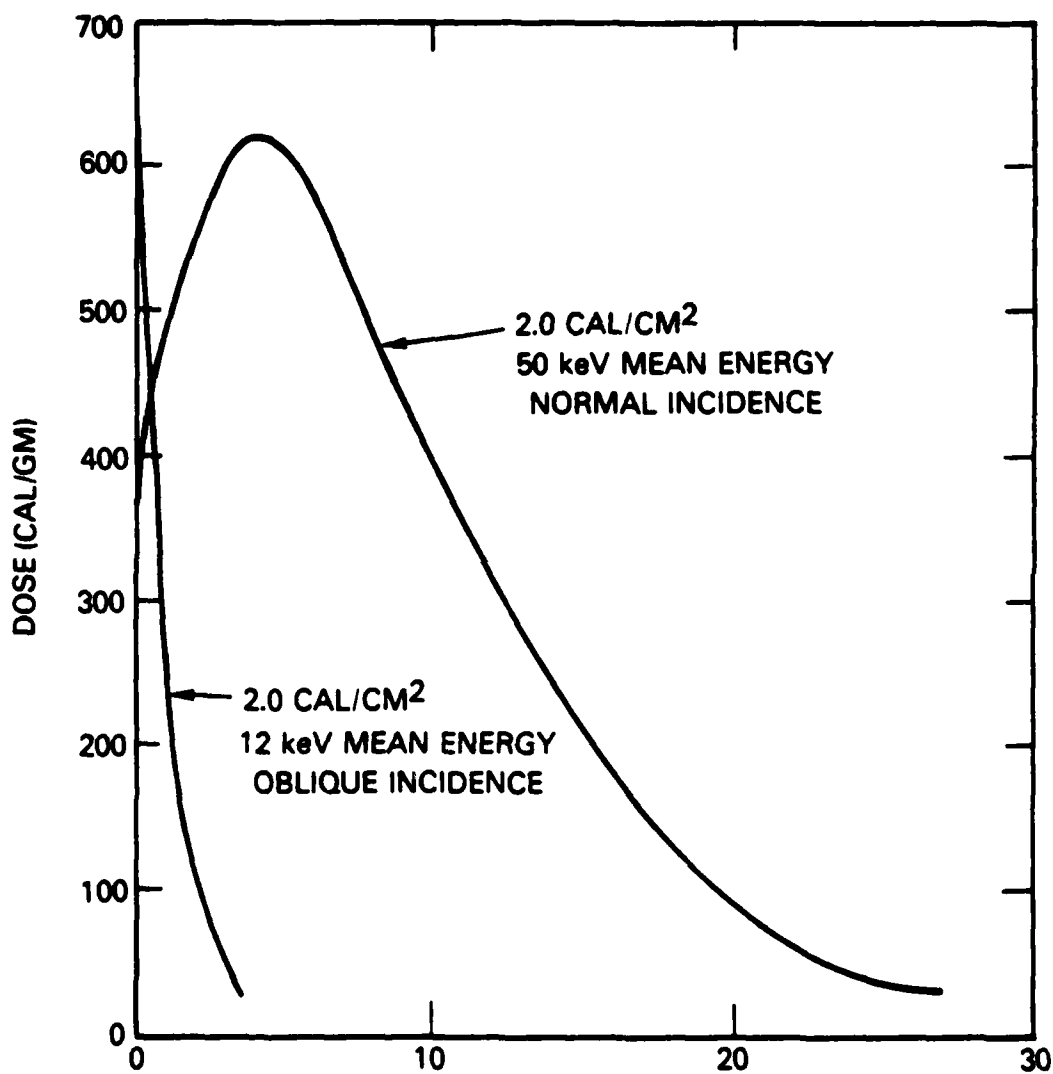


Fig. 2 - Energy deposition profile for an electron beam incident on silicon. (15)

phase by an energetic ion does, however, provide an important instance where improved understanding of physics of rapid heating and cooling is needed. Current thinking on ion penetration visualizes a thermal spike, i.e., the ion passage creates a small, very hot zone. This rapidly quenches. Optical and massive emissions from this hot zone provide the basis for several poorly understood surface analytical tools — SIMS and IIR. In the bulk, the results of the quenching process lead to the presence (or absence) of radiation damage. It is well known that the damage in metals is less than in covalent materials; this should be directly related to the observations made on growth kinetics in Section II.A.1.b. A better understanding of the microscopic aspects of energy transport between incident ion and the target material is critical to better understanding of the damage and emission.

2. Thermalization Processes: T_1 , T_2

a. Electron-Phonon Thermalization (T_1)

Both electron and phonon beams (for those materials with strong optical absorption) are believed to couple their energy directly into the electron manifold of the material under irradiation. The energy will rapidly thermalize within the electron manifold (electron-electron T_2) and is believed to transfer into the phonon system (electron-phonon T_1) in a time scale on the order of picoseconds. For most of the materials processing work, these time scales are sufficiently rapid to safely presume the validity of a local material temperature. For picosecond and faster pulses, it has been suggested that it might be possible to observe the electron-phonon T_1 process.⁽¹⁶⁾ This possibility has been tested once for metals at room temperature and no evidence was found for

a departure from thermal equilibrium between conduction electron and lattice phonons.⁽¹⁾ Low temperature experiments, where the relaxation times are longer, would be interesting, as would investigation of semiconductors.

b. Phonon-Phonon Thermalization (T_2)

At room temperature the establishment of thermal equilibrium within the phonon system is believed to occur on the order of 10^{-12} sec or faster. At lower temperatures thermalization processes can become considerably longer. In particular, the umklapp processes can be frozen out for $T < \Theta_D$ and the thermal conductivity considerably increased. Rapid heating leading to a moderate temperature rise might be used to study thin film thermal conductivity in the regime where phonon mean-free paths were large. If non-thermalized phonons were created at a surface, the relationship between conductivity and thermalization might be explored.

3. Interfacial Energy Transfer

a. Solid-Gas

Studies of the solid-gas interface are key to the understanding of microscopic energy transfer mechanisms across an interface because there exist analytical tools which can characterize the nature of the interface. Rapid heating could be used to produce temperature jumps at a solid-gas phase interface which could result in new reaction and desorption mechanisms that would not happen with slower heating rates. Or the wavelength selectivity of the laser might be used to pump energy in specific vibrational or electronic levels of adsorbed species.

From a different vantage point, the energy accommodation by the surface of an impinging gas molecule can be thought of as a rapid cooling

process. The accommodation is of interest, not only from the macroscopic aero- and hydrodynamic considerations, but also because it can be used to study the processes which happen at the liquid/solid interface during melting or solidification and at the solid/gas interface during MBE. While elastic atomic scattering has a reasonably large group of investigators amongst surface scientists, the study of inelastic scattering and accommodation has a limited following.

b. Solid-Solid and Solid-Liquid

The transfer of energy across an interface is represented in the macroscopic world as a thermal impedance. The microscopic description of this impedance is a difficult problem. Studies of fast transient response and large perturbations might lead to new insights. The heat transfer process across the solid-liquid interface must be ultimately bound up with the resolidification process since the atomic motions at the interface determine both. This topic would be very important to studies of rapid heating/cooling of optically transparent media where a surface film could be used to absorb the energy from a laser beam and transmit it to the substrate.

4. Thermoelectric Effects

The temperature gradients available via rapid heating and cooling can be 10^7 °K/cm. Would this be reflected in voltage transients via the Seebeck effect? Could a direct measure of the transient surface temperature gradients be derived from those voltages?

5. Thermo-Acoustic Coupling

The common treatment of photon and electron coupling to a solid has the energy absorbed by the substrate electrons and transmitted

as thermal energy to the phonon system. Some of that energy, if only through thermal expansion, must be coupled into acoustic emission. What information is available in that emission? If the absorbed energy is sufficient, then the acoustic response of the solid may be in the form of a shock wave. Under what conditions will that prevail? Work at Lawrence Livermore Laboratory has shown shock velocities consistent with 20-25 Mbar in aluminum; this pressure is nearly an order of magnitude greater than achieved by more conventional laboratory techniques.⁽¹⁷⁾

C. Theoretical Concepts

There is need for theoretical work in all of the areas covered in the opportunities section. One particular issue which merits specific mention is an examination of the meaning of temperature and heat flow in the presence of very large temperature gradients. The gradients cited in the literature^(1,18) are reaching $dT/dx \sim 10^7 - 10^8$ °K/cm (see Figure 3). This implies a variation of 0.3 °K per atomic separation and a variation of 3°K per phonon mean-free path at room temperature. Do the classical, macroscopic heat flow equations have any validity under these conditions? What happens for picosecond and faster pulses where the gradient may be even larger?

D. Dynamic Analytical Capability

In order to evaluate the dynamics of the rapid heating/cooling research opportunities, it is necessary to have analytical tools which can measure the appropriate physical properties on a fast time scale. Otherwise, analysis of quenched systems will be required, where one works on the premise that relevant information can be frozen in place by the rapid cooling. The development of these dynamic analytical tools should

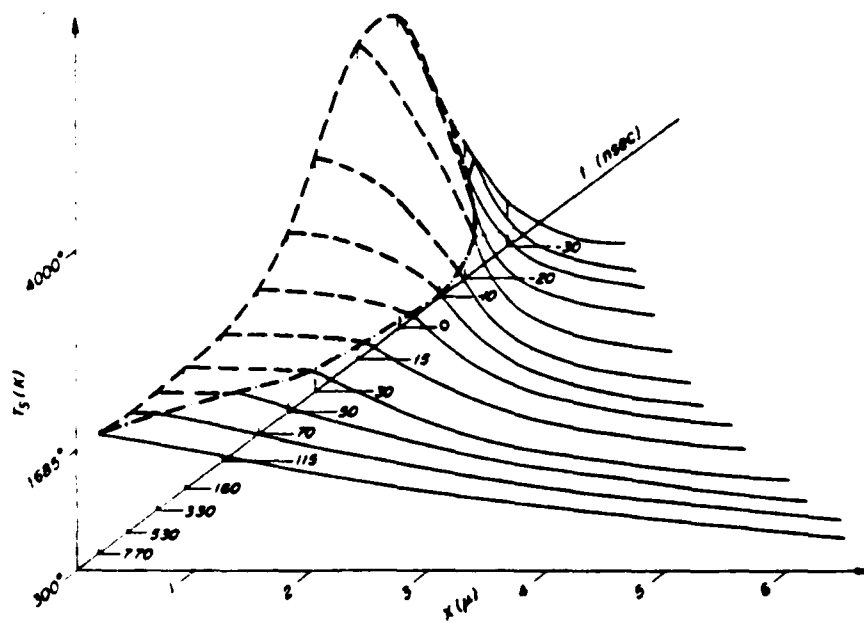


Fig. 3 - Calculated temperature profiles as a function of time for a 0.53μ , $4.5\text{J}/\text{cm}^2$, 33 nsec pulsed laser beam incident on silicon. (18) The temperature gradient in the vicinity of the peak temperature is $\Delta T/\Delta X \sim 10^3/10^{-4} = 10^7 \text{ }^\circ\text{K}/\text{cm}$.

not be the main thrust of a rapid heating/cooling program, but opportunities to make significant advances should be exploited, especially in conjunction with the study of the time evolution of an important physical property in rapid heating/cooling.

In the area of temperature measurement, such phenomena as optical emission, thermionic emission, and thermoelectric transients offer possibilities. A mechanism to determine transient or steady state temperature profiles in thin surface layers would be extremely valuable; for instance, it might be possible to build a microscope which could view emission from the side of a sample being heated on its front face. The exploration of chemical kinetics has possibilities via fast optical spectroscopies such as absorption, Raman, and laser induced fluorescence. Structural information might be available via pulsed X-ray sources.

III. CONCLUSIONS AND RECOMMENDATIONS

1. In the course of gathering information for this report, the author took the opportunity to speak with several of the major investigators in the field. There was agreement that physics research opportunities exist and that the technology for achieving rapid heating/cooling were sufficiently developed to begin to exploit those opportunities. While everyone expressed an interest in exploring the physics as well as the materials questions, many investigators were so enmeshed in materials research that they had some difficulty reorienting their thinking to a physics perspective. An ONR physics program in rapid heating and cooling will have to be carefully defined and publicized so that proposals submitted to the program are not materials research. This argues for a modest start, with the program building momentum in succeeding years. A good advertising effort will be very important in order to alert the community to the availability of support and the desired program goals.

2. The exploration of physics issues via rapid heating/cooling will require the coordination of at least two areas of expertise -- those associated with the pulsed sources of energy and its interaction with matter and those knowledgeable with the specific physics issue of interest. To this, one might add another necessary area of expertise; i.e., those knowledgeable in either dynamic analytical measurements or in analysis of the properties of thin films. The necessary marriage of two or three specialties argues for larger contracts at institutions with the required expertise. It also suggests that national rapid heating/cooling centers, with requisite energy sources and diagnostics, be established and made available to investigators wishing to explore a physics research problem.

3. The physics research and materials research in rapid heating and cooling are supportive. The materials research provides a large technology base, a scientific community, and new poorly understood phenomena, particularly at the microscopic level. ONR Codes 471 and 427 presently support research in rapid heating and cooling.

4. Further exploration of the rapid heating/cooling possibilities is sure to sharpen the ideas presented here and to expand the possibilities. Certainly this brief does not encompass all possibilities. For instance, no mention has been made of rapid temperature changes as a mechanism to examine cooperative phenomena with critical temperatures such as ferromagnetism or superconductivity.

REFERENCES

1. N. Bloembergen in Laser Solid Interactions and Laser Processing - 1978, S. D. Ferris, H. J. Leamy and J. M. Poate, eds., AIP Conference Proceedings No. 50 (1979), page 1.
2. H. A. Davies in Rapidly Quenched Metals III, Vol. 1, Proceedings of Third International Conference on Rapidly Quenched Metals, B. Cantor, ed., The Metals Society, London (1978), page 1.
3. H. Reiss and J. L. Katz in Rapid Solidification Processing, Proceedings of International Conference on Rapid Solidification Processing, R. Mehrabian, B. H. Kear, and M. Cohen, eds. (Claitor Publishing Division, Baton Rouge, 1978), page 64.
4. F. Spaepen and D. Turnbull in Laser Solid Interactions and Laser Processing - 1978, S. D. Ferris, J. H. Leamy, and J. M. Poate, eds., AIP Conference Proceedings No. 50 (1979), page 73.
5. K. A. Jackson and J. H. Leamy in Laser Solid Interactions and Laser Processing - 1978, S. D. Ferris, J. H. Leamy, and J. M. Poate, eds., AIP Conference Proceedings No. 50 (1979), page 102.
6. M. Hillert and B. Sundman, Acta Metallurgica 25 11-18 (1977).
7. W. L. Johnson in Rapidly Quenched Metals III, Vol. 2, Proceedings of Third International Conference on Rapidly Quenched Metals, B. Cantor, ed., The Metals Society, London (1978), page 1.
8. Chemical and Engineering News, September 17, 1979, page 21.
9. G. J. Abbaschian in Rapid Solidification Processing, Proceedings of International Conference on Rapid Solidification Processing, R. Mehrabian, B. H. Kear, and M. Cohen, eds. (Claitor Publishing Division, Baton Rouge, 1978), page 84.
10. N. G. Ainslie, J. D. MacKenzie and D. Turnbull, J. Phys. Chem. 65 1718 - 1724 (1961).
11. J. D. Ayers and T. B. Massalski, Metal Trans. 3, 261-271 (1972).
12. R. M. Walser and M. F. Becker in Laser Solid Interactions and Laser Processing - 1978, S. D. Ferris, J. H. Leamy, and J. M. Poate, eds., AIP Conference Proceedings No. 50 (1979), page 117.
13. "Laser Ignition of Solid Propellant Formulations," Geo-Centers Inc., Final Report to U.S. Army Armament R&D Command on Contract No. DAAK-10-79-M-2239, June 1979.

14. S. S. Lau, W. F. Tseng, I. Golecki, E. F. Kennedy and J. W. Mayer in Laser Solid Interactions and Laser Processing - 1978, S. D. Ferris, H. J. Leamy, and J. M. Poate, eds., AIP Conference Proceedings No. 50 (1979), page 503.

15. A. R. Kirkpatrick, A. C. Greenwald, J. A. Minnucci, and R. G. Little in Laser Solid Interactions and Laser Processing - 1978, S. D. Ferris, H. J. Leamy, and J. M. Poate, eds., AIP Conference Proceedings No. 50 (1979), page 475.

16. S. I. Anisimov, B. L. Copelivich, and T. L. Perelman, Sov. Phys. - JETP 39, 375 (1974).

17. H. P. Holmes, R. J. Trainor, R. M. More, and R. A. Anderson, "Laser Generated Shock Wave Experiments at Pressures Above 1 TPa". Abstracts of 1979 IEEE/OSA Conference on Laser Engineering and Applications, Washington, D. C. (1979).

18. C. M. Surko, A. L. Simons, D. H. Auston, J. A. Golovchenko, R. E. Slusher and T. N. C. Verkatesan in Laser Solid Interactions and Laser Processing - 1978, S. D. Ferris, J. H. Leamy, and J. M. Poate, eds., AIP Conference Proceedings No. 50 (1979), page 155.